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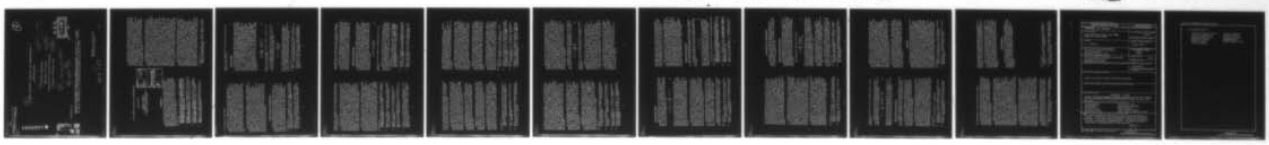

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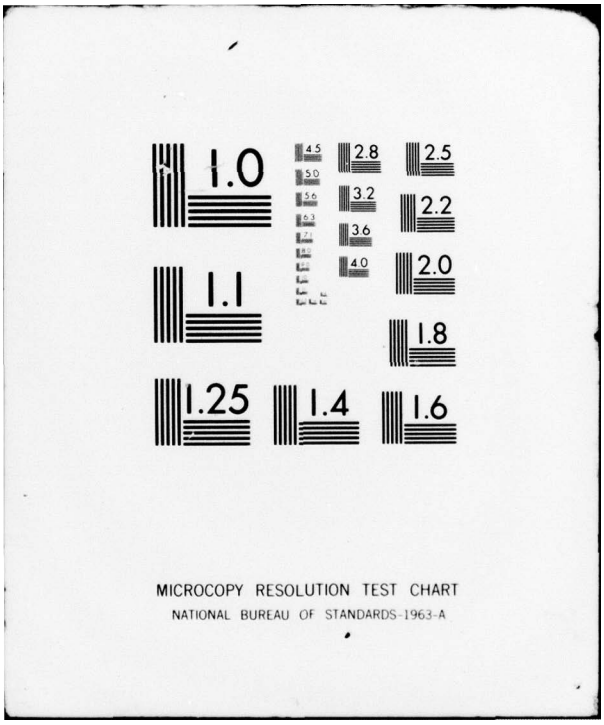
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BASIC CONCEPTS OF ELECTRO- AND THERMOMIGRATION; DRIVING FORCES.

Richard S. Sorbello
Department of Physics
University of Wisconsin-Milwaukee
Milwaukee, Wisconsin 53201

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BASIC CONCEPTS OF ELECTRO- AND THERMOMIGRATION;

DRIVING FORCES

Richard S. Sorbello
Department of Physics
University of Wisconsin-Milwaukee
Milwaukee, Wisconsin 53201

Introduction

In the past few years considerable progress has been made in understanding atomic migration in electric fields and thermal gradients. Specifically, the microscopic nature of the driving forces for atomic migration has been clarified and new theoretical concepts have been introduced. We shall discuss these new developments and indicate some promising new areas for further research. Recent discussions on the subject may be found in the Proceedings of the Yorktown Heights Conference (1) and in review papers by Huntington (2,3) and the author (4).

1. Gangulee, A., Ho, P.S. and Tu, K.N., editors, Proceedings of the International Conference on Low Temperature Diffusion and Application to Thin Films, Elsevier Sequoia, Lausanne, 1975. (Also reported in Thin Solid Films, Vol. 25, 1975, pp. 1-552.)

2. Huntington, H.B., "Electro- and Thermomigration in Metals", in ASM Seminar Book on Diffusion, Aaronson, H.I., editor, American Society for Metals, Metals Park, Ohio, 1974, pp. 155-184.

3. Huntington, H.B., "Electromigration in Metals", in Diffusion in Solids: Recent Developments, Nowick, A.S. and Burton, J.J., editors, Academic Press, New York, 1974, pp. 303-352.

4. Sorbello, R.S., "Theory of Electromigration in Metals", Comments on Solid State Physics, Vol. 6, 1975, pp. 117-122.

The quantities of interest are the transport coefficients relating the atom (or ion) flux $\vec{J}$ with the applied field $\vec{E}$ and with the applied thermal gradient $\vec{\nabla}T$. For the case of electromigration or atomic migration in electric fields, we can write (for $\vec{\nabla}T = 0$) the relation $\vec{J} = \overleftrightarrow{L}_E \cdot \vec{E}$ where the tensor $\overleftrightarrow{L}_E$ is the transport coefficient of interest. For thermomigration, or atomic migration in a thermal gradient we can write (for $\vec{E} = 0$) the relation $\vec{J} = \overleftrightarrow{L}_T \cdot (\vec{\nabla}T/T)$ where $\overleftrightarrow{L}_T$ is the transport coefficient of interest and T is the temperature. In the usual case, $\vec{E}$ and $\vec{\nabla}T$ are sufficiently small that $\vec{J}$ will be linear in $\vec{E}$ or $\vec{\nabla}T$ and hence $\overleftrightarrow{L}_E$ and $\overleftrightarrow{L}_T$ are independent of $\vec{E}$ and $\vec{\nabla}T$.

In principle one could calculate $\overleftrightarrow{L}_E$ and $\overleftrightarrow{L}_T$ directly from a full quantum mechanical formalism in which transition rates of atoms are calculated in the presence of $\vec{E}$ or $\vec{\nabla}T$ and any electron and phonon currents caused by $\vec{E}$ or $\vec{\nabla}T$. However the calculation of migration rates is simplified considerably if it is permissible to introduce the idea of a microscopic driving-force acting on the atoms. The picture of atomic migration then separates into two parts: first, the calculation of the microscopic force arising from $\vec{E}$ or $\vec{\nabla}T$ and the electron and phonon currents; and, second, the response of the atoms to the microscopic force. In the simple case of interstitial diffusion, for example, one would first determine the microscopic force $\vec{F}$ exerted on the atom. The atomic current is then obtained from the relation $\vec{J} = \mu\vec{F}$ where μ is the atomic mobility. μ is related to the diffusion coefficient D by means of the Nernst-Einstein relation $\mu = cD/k_BT$ where c is the concentration of impurities and k_B is Boltzmann's constant. For more general diffusion mechanisms, the Nernst-Einstein relation may have to be modified to include correlation and vacancy-flow effects (5). In general, since $\vec{F}$ will depend on the atomic position, an average of $\vec{F}$ will be needed over the diffusion jump path.

The introduction of a microscopic force-field $\vec{F}$ is difficult to justify for the contribution of phonon currents to thermomigration. The problem here is that the dynamics of the jumping atom are not generally separable from the phonon dynamics. However, for the electronic contributions to electro- and thermomigration the use of $\vec{F}$ is justifiable. The point is that the electrons are much lighter than the ions and follow the ions adiabatically throughout the jump process. We can therefore regard the migrating atom to be a heavy, very slowly moving ion interacting with a quantum mechanical gas of electrons. This picture is just an application of the usual Born-Oppenheimer adiabatic approximation. By invoking this approximation we do not restrict ourselves to classical atomic motion since $\vec{F}$ defines a potential energy field which may be used in a full quantum mechan-

5. Howard, R.E. and Lidiard, A.B., "Matter Transport in Solids", Reports on Progress in Physics, Vol. 27, 1964, pp. 161-240.

ical calculation of atomic motion.

The force $\vec{F}$ is defined as the time rate of change of the momentum of the ion. (The force is not the energy derivative with respect to ion coordinate since the system is open.) We remark that ion recoil in the scattering of electrons by the impurity ion can be neglected in computing $\vec{F}$. Recoil events do not need to be considered because electron-ion scattering is predominantly elastic (6). It may seem paradoxical that we ignore the recoil of the ion since without recoil the ion would not move and atomic migration would not occur. Recall, however, that we are using the adiabatic approximation only to compute a force field. The ionic motion enters at a later stage because of the large inertia of the ions.

An alternate physical viewpoint is to imagine holding down the ion at some point in the equilibrium lattice with a very strong spring and to associate the driving force with the amount of stretching of the spring when the field is turned on and the impurity is pushed against the spring. The amount by which the spring is stretched in going to its new equilibrium position corresponds to some force $\vec{F}'$ which would have to be applied to the impurity on the spring in the absence of the external field. Using the fact that the time rate of change of impurity momentum is zero in the new equilibrium position, we find (7) that $\vec{F}' = \vec{F}$. This implies that an impurity tied down to the lattice does feel a force exactly equal to the value $\vec{F}$ which we previously calculated from the rate of change of momentum.

Driving Force for Electromigration

It has long been recognized that there are two distinct contributions to the force $\vec{F}$ on an impurity. One is due to the direct external field $\vec{E}$ acting on the impurity ion. This contribution is called the direct electrostatic force, and we denote it by $\vec{F}_{es}$. It includes the applied force $Ze\vec{E}$ on the bare ion of valence Z and any additional electrostatic shielding effects due to the electrons surrounding the ion. (Here e is the charge of a proton). The second contribution to $\vec{F}$ arises from momentum transfer by the electron current as electrons collide with the

6. Sorbello, R.S., "A Pseudopotential-based Theory of the Driving Forces for Electromigration in Metals", Journal of Physics and Chemistry of Solids, Vol. 34, 1973, pp. 937-950.

7. Sorbello, R.S., "Contribution to Atomic Migration in Metals from Electron and Phonon Scattering", Ph.D. Thesis, Stanford, 1970 (Abstracted in Dissertation Abstracts International, Vol. 31, No. 11, 1971).

impurity. This contribution is called the electron-wind force, and we denote it by $\vec{F}_{wd}$.

Ballistic Models

In the early ballistic theories by Fiks (8) and by Huntington and Grone (9) it was assumed that electrostatic shielding of the impurity ion was negligible, and therefore $\vec{F}_{es} = Ze\vec{E}$. The electron-wind force was determined by calculating the momentum transfer per second by the electrons to a defect consisting of an isolated impurity. The electrons were considered in the free-electron gas model. The results can be understood from the fact that the momentum lost per second by an electron in scattering by defects is $m\vec{v}_D/\tau_d$ where m is the electron mass, $\vec{v}_D$ is the drift velocity of the electrons, and τ_d is the collision time for electron scattering with the defects. The net momentum lost per second per unit volume by the electrons to impurity defects is then $nm\vec{v}_D/\tau_d$ where n is the electron density. The force on a single defect is therefore $nm\vec{v}_D/\tau_d N_d$ where N_d is the density of defects. Since the electron current $\vec{j}$ equals $-ne\vec{v}_D$ we can re-write this electron-wind force as

$$\vec{F}_{wd} = \frac{-\vec{j}m}{e\tau_d N_d} = -e\left(\frac{\rho_d}{N_d}\right)\left(\frac{n}{\rho}\right)\vec{E} \qquad (1)$$

where $\rho = E/j$ is the total resistivity and $\rho_d = m/ne^2\tau_d$ is the resistivity due to defects.

It is customary to express the total force $\vec{F} = \vec{F}_{es} + \vec{F}_{wd}$ in terms of an effective valence Z^* which is defined such that $\vec{F} = Z^*e\vec{E}$. The ballistic theories therefore yield

$$Z^* = Z - Z_o\left(\frac{\rho_d}{N_d}\right)\left(\frac{N}{\rho}\right) \qquad (2)$$

where the density of background atoms is N and their valence is Z_o. A dilute concentration of impurities has been assumed in obtaining equation (2) from equation (1) since we have used $n = NZ_o$. Subsequent generalizations of equation (2) were made for solids in which the free carriers are holes rather than

8. Fiks, V.B., "On the Mechanism of the Mobility of Ions in Metals", Soviet Physics - Solid State, Vol. 1, 1959, pp. 14-28.

9. Huntington, H.B. and Grone, A.R., "Current Induced Marker Motion in Gold Wires", Journal of Physics and Chemistry of Solids, Vol. 20, 1961, pp. 76-87.

electrons (10). The result is that the sign is changed for the electron-wind contribution (ie., the second term on the right-hand side of equation (2)).

It has proven difficult to generalize the ballistic theories with any degree of rigor to include band structure effects and more complicated defect scattering than isolated impurities. The problem is that the momentum lost by the electrons does not go to only the particular atom of interest. Some momentum goes to the lattice and some goes to the neighboring scatterers, e.g., other impurities and vacancies. The amount of momentum transfer partitioned between the lattice and a single free (non-localized) impurity traveling through a perfectly regular lattice has been determined (11). It turns out that the momentum transferred to the impurity equals the pseudo-momentum lost by the electrons in scattering. Unfortunately the methods used to derive this result preclude any application to a localized defect complex.

While equation (2) has met with considerable criticism, there seems to be a growing consensus that it is essentially correct for the simple model for which it was originally derived, namely a dilute concentration of random impurities in a free electron gas in which there also exists a structureless background scattering mechanism such as phonons. In this model the background lattice atoms are replaced by a uniform positive charge ("jellium"). For this model and assuming only one impurity species, results equivalent to equation (2) have been derived from semi-classical momentum balance considerations by Landauer (12) and Sham (13). A rigorous verification of equation (2) was outlined by the author (4,14) for

10. Huntington, H.B. and Ho, S.C., "Electromigration in Metals", Journal of the Physical Society of Japan, Vol. 18, Supplement II, 1963, pp. 202-208.

11. Kagan, M.I., Lifshitz, I.M. and Fiks, V.B., "Electron Scattering by Impurity Centers", Soviet Physics-Solid State, Vol. 6, 1965, pp. 2167-2170.

12. Landauer, R., "The Das-Peierls Electromigration Theorem", Journal of Physics C, Vol. 8, 1975, pp. L389-L391.

13. Sham. L.J., "A Microscopic Theory of the Driving Force in Electromigration", Physical Review B, Vol. 12, 1975, pp. 3142-3149.

14. Sorbello, R.S., "New Developments in Electromigration", unpublished paper presented at Electromigration Workshop at conclusion of the International Conference on Low Temperature Diffusion and Application to Thin Films, Yorktown Heights, August 15, 1974.

the simpler model in which there are no additional scattering mechanisms other than the dilute random impurities in "jellium".

A successful generalization of the ballistic theory has been made by Feit (15). Starting from a quantum-mechanical expression for the rate of momentum change, Feit obtained an expression for the amount of momentum transfer to be associated with each collision of the electrons with the impurity. Although this procedure seems difficult to justify rigorously, it can be understood (4) from the polarization charge model of Bosvieux and Friedel (16).

Polarization-charge Models

Bosvieux and Friedel (16) presented an alternate method for calculating the force on an ion. They realized that the force $\vec{F}$ is identical to the electrostatic force exerted by the exact electron charge density on the bare ion. This result, which for closed systems is known as the Feynman-Hellman theorem, is easy to show from the definition of $\vec{F}$ within the adiabatic approximation (see, for example (4) and (17)). Specifically, if $\delta n(\vec{r})$ is the part of the electron density which depends on the electric field and current, one can use the operator equation of motion for the ion momentum and obtain

$$\vec{F} = Ze\vec{E} - \int \delta n(\vec{r}) \frac{\partial V}{\partial \vec{R}} d^3r \qquad (3)$$

where V is the bare electron-ion interaction and $\vec{R}$ is the ion position.

Equation (3) is exact for the time rate of change of ion momentum. If the ion is taken to be a free non-localized particle, its rate of momentum change computed by the ballistic model must be the same as $\vec{F}$ given by equation (3). In classical terminology, this equivalence arises because the average force exerted by the

15. Huntington, H.B., Alexander, W.B., Feit, M.D. and Routbort, J.L., "Anisotropy in Electromigration", in Atomic Transport in Solids and Liquids, Lodding, A. and Lagerwall, T., editors, Verlag der Zeitschrift fur Naturforschung, Tubingen, 1971, pp. 91-96.

16. Bosvieux, C. and Friedel, J., "Sur L'Electrolyse des Alliages Metalliques", Journal of Physics and Chemistry of Solids, Vol. 23, 1962, pp. 123-136.

17. Kumar, P. and Sorbello, R.S., "Linear Response Theory of the Driving Forces for Electromigration", Thin Solid Films, Vol. 25, 1975, pp. 25-35.

ion on an electron moving along some trajectory is the same as the time rate of change of the electron's momentum. The equivalence between ballistic and charge-polarization models has been explicitly verified for $\vec{F}_{wd}$ in the free-ion model.

The Bosvieux-Friedel calculations were extended by Gerl (18) and later applied to more realistic models of metals using pseudopotential theory (6). The basic picture is that the electron-wind force $\vec{F}_{wd}$ arises from dipolar charge distributions around every defect in the crystal. For isolated impurities equation (2) is recovered. For more complicated scattering centers there is substantial interference from neighboring atoms and $\vec{F}_{wd}$ is not simply related to the defect resistivity. In fact the interference from neighboring atoms may reverse the direction of $\vec{F}_{wd}$.

The pseudopotential calculations gave reasonable over-all agreement with experimental values of Z^* (6). The general expression when applied to liquid metals gives a formula which was independently obtained by Faber (19) using a heuristic argument. Using this formula, Stroud obtained reasonable agreement with experiment (20).

Extension of the pseudopotential calculations to more complicated systems, including grain boundaries and dislocations would seem promising. To obtain numerical values for $\vec{F}_{wd}$ one need only place the atoms in the desired configuration and evaluate a simple integral for the two-body force due to the dipolar charge distributions interacting between neighboring defects (6).

It was shown (6) that in the pseudopotential model $\vec{F}_{wd}$ is derivable from a scalar potential. $\vec{F}_{wd}$ is thus a conservative force provided that the neighboring ions remain fixed. The point is that the force on any ion is sensitive to the other ions around it and hence will be different depending on the way neighboring ions move in the diffusion-jump process. Such a configuration dependent force has been suggested as a possible explanation of

18. Gerl, M., "Calculation of the Force Acting on an Impurity in a Metal Submitted to an Electric Field or a Temperature Gradient", in Atomic Transport in Solids and Liquids, pp. 9-17.

19. Faber, T.E., Theory of Liquid Metals, Cambridge University Press, Cambridge, 1972.

20. Stroud, D., "Calculations of the Average Driving Force for Electromigration in Liquid-Metal Alloys", Physical Review B, Vol. 13, 1976, pp. 4221-4226.

recent electromigration data on fast diffusers (21). Configurational effects may also help us understand the reversals observed (22) for electromigration in grain boundaries. In treating grain-boundaries it may prove useful to try to apply the Feit expression (16) since it extends the pseudopotential results (6) to include additional band-structure effects which may be important.

One of the more controversial points in the Bosvieux-Friedel treatment is their treatment of the direct field force $\vec{F}_{es}$. They found that for an interstitial impurity $\vec{F}_{es} = 0$; that is, the ion is completely shielded. In terms of equation (3), this means that a static shielding contribution to δn cancels the bare $Ze\vec{E}$ contribution. The Bosvieux-Friedel derivation has not been generally accepted, however, since it appears that their derivation of $\vec{F}_{es}$ requires that no electron transport be allowed. Moreover, it seems not to consider explicitly the force exerted on the additional electrons brought in by the impurity when it is dissolved in the metal.

There has been considerable controversy about the various contributions to δn in equation (3). Landauer and Woo (23) argue that in addition to the electrostatic shielding charge (associated with $\vec{F}_{es}$) and the Bosvieux-Friedel (BF) dipolar charge (associated with $\vec{F}_{wd}$) other sources are present. These sources are the very localized charge density at the impurity caused by Landauer's (24) "residual resistivity dipoles" (RRD), and the "carrier-modulation effect".

The RRD represents electronic charge which forms around the impurity so as to provide the additional field needed to drive the electron current around the impurity. The RRD field is second-order in the scattering potential, V, unlike the field of the BF dipoles which is first order in V. However according to Landauer and Woo (23) the net force from the RRD at the bare ion is of the same order as the BF or ballistic $\vec{F}_{wd}$ of equation (2). (Of course,

21. Hsieh, M.Y., Huntington, H.B. and Jeffery, R.N., "Electromigration of Au and Ag in Lead", to be published.

22. Gangulee, A. and d'Heurle, F.M., "Electromigration and Transport Reversal in Copper-Silver Thin Films", Journal of Physics and Chemistry of Solids, Vol. 35, 1974, pp. 293-299.

23. Landauer, R. and Woo, J.W.F., "Driving Force in Electromigration", Physical Review B, Vol. 10, 1974, pp. 1266-1271.

24. Landauer, R., "Spatial Variation of Currents and Fields Due to Localized Scatterers in Metallic Conduction", IBM Journal of Research and Development, Vol. 1, 1957, pp. 223-231.

the RRD-field is along $\vec{E}$, however.) Now even if the RRD are as localized as claimed by Landauer and Woo, the effect of the RRD-field is still not obvious, since there may be an additional screening field around the bare ion in response to the RRD-field, just as there is in response to the BF dipoles. In the latter case, the additional screening field has the effect of dressing the bare ion so that the net force is given by the BF dipole acting on the screened ion and not the bare ion. Unfortunately, the BF-calculation is a self-consistent screening calculation linear in V and is not readily generalized to treat RRD-fields which are quadratic in V. This makes some arguments (25) based on linear dielectric-screening unconvincing. Similarly, the first-order fully semi-classical calculation of Das and Peierls (26) cannot deal with RRDs.

The "carrier-density modulation" (CDM) effect arises from the changed carrier density in the vicinity of the impurity. The density is increased for an attractive potential since electrons are drawn to the impurity. The reverse occurs for repulsive potentials. This density change will effect the field by making it easier or harder to overcome lattice scattering. Landauer and Woo (23) insisted that the CDM-effect was included in the Das-Peierls (26) analysis, and in a recent paper, Das and Peierls finally agreed (27).

A remarkable situation has developed in which the protagonists in the polarization-charge debate -- Landauer, Das and Peierls, Gerl, and Sham, as well -- have reached the same result for the model system of dilute impurities in "jellium" with a uniform background scattering. Their result essentially is -- mirabile dictu -- the ballistic model expression, equation (2). Strangely, however, Gerl and coworkers (28) deny that their result is equivalent to the ballistic result, but instead, claim that their result verifies the BF result that $\vec{F}_{es} = 0$ and that only the electron-wind force given by equation (1) is present.

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25. Turban, L. and Gerl, M., "Driving Force in Electromigration and the Residual Resistivity Field", Physical Review B, Vol. 13, 1976, pp. 939-942.

26. Das, A.K. and Peierls, R., "The Force on a Moving Charge in an Electron Gas", Journal of Physics C, Vol. 6, 1973, pp. 2811-2821.

27. Das, A.K. and Peierls, R., "The Force in Electromigration", Journal of Physics C, Vol. 8, 1975, pp. 3348-3351.

28. Turban, L., Nozieres, P., and Gerl, M., "Driving Force for the Electromigration of an Impurity in an Homogeneous Metal", Journal de Physique, Vol. 37, 1976, pp. 159-164.

The source of this apparent misunderstanding seems to lie in the definition of $\vec{F}_{wd}$. For the simpler model in which uniform background scattering is missing, Sorbello (4,14) has shown that the exact Z^* can be put into a form like equation (2) or into a form in which only a term resembling the electron-wind contribution, i.e., the second term of equation (2), is present. This result was derived by noting that the expectation value of the rate of change of the total electron momentum vanishes in the steady state and writing out this commutator explicitly using the full hamiltonian. It immediately follows that the net force exerted by $\vec{E}$ on the electrons is exactly the force transmitted by the electrons to the impurity ions. The final expressions given in (4) show that $\vec{F}$ contains the ZeE term although $\vec{F}$ can be cast into a form where this term seems to disappear.

An analogous situation occurs for the model in which there is also the additional background scattering present. The result for that model is (12,13,27,28) $\vec{F} = -Z_o e(N/N_d)(\Delta\rho/\rho)\vec{E}$ which implies

$$Z^* = - Z_o \left(\frac{\Delta\rho}{N_d}\right)\left(\frac{N}{\rho}\right) \qquad (4)$$

where $\Delta\rho = \rho - \rho_o$ is the change in resistivity caused by introducing impurities, and ρ_o is the resistivity in the absence of impurities.

Equation (4) is not the same as the wind contribution in equation (2), because $\Delta\rho \neq \rho_d$. The point is that there is a contribution to $\Delta\rho$, which can be thought of as a kind of average CDM-effect, due to the additional electrons contributed to the conduction band by the impurities. This will change the effect of the background resistivity but does not appreciably effect ρ_d since ρ_d arises from defect scattering. Since the additional electrons change the resistivity by an amount $-(\Delta n/n)\rho_o$ where Δn is the change in electron density due to the impurity electrons, we can write $\Delta\rho = \rho_d - (\Delta n/n)\rho_o$ and use the fact that $\Delta n/n = ZN_d/Z_o N$ to recover equation (2) from equation (4) to excellent accuracy.

This discussion indicates that the BF result that $\vec{F}_{es}$ vanishes is incorrect because it does not take Δn into account. Landauer (12) and Das-Peierls (27) refrain from putting equation (4) into the form of equation (2) presumably because of other possible field inhomogeneities which may be present in the semi-classical picture. Nonetheless, the connection between equations (4) and (2) is implied. The linear response calculation and discussion of Sham (13), however, does make it clear that the equations (4) and (2) are essentially identical.

Linear Response Theory

Semiclassical models are of limited validity for atomic-scale phenomena. For this reason, and to establish a rigorous framework for treating electric field and current effects, Kumar and Sorbello (17) introduced a linear-response theory of electromigration. Using the Kubo formulation, they derived the following exact result for the i-th component of $\vec{F}$ (17):

$$F_i = ZeE_i + e << \frac{\partial V}{\partial R_i} ; \vec{r} >> \cdot \vec{E} \qquad (5)$$

where $\vec{r}$ is the electron-coordinate operator, and the brackets indicate a correlation function in the equilibrium lattice in the absence of the applied field. All electron-wind and electrostatic shielding effects are contained in this force-velocity correlation function. Kumar and Sorbello (17) evaluated this correlation function using a "memory-function" formalism and were able to reproduce the earlier pseudopotential result (6). They also applied equation (5) to surface electromigration. For weak scatterers they found that there is no additional electrostatic shielding of the ion.

The recent evaluation of equation (5) by Sham (13) is the most satisfactory to date since it treats fully interacting electrons in a periodic lattice and in the presence of strong impurity scattering. Sham's result indicates that the electron-electron interaction essentially just screens the ion potential in the impurity scattering T-matrix. Diagrammatic interpretation is made of the RRD and CDM. These effects are apparently absorbed in the scattering cross-section corresponding to the electron-wind term. There is no additional explicit shielding of $\vec{E}$.

For weak scatterers, Sham recovers the result of Feit (15), and, if the lattice potential is ignored, the earlier ballistic and charge-polarization results. The Landauer RRD and CDM effects will only have an effect if the Born-approximation is not valid -- i.e., if the scattering is strong. However, they need not be explicitly considered if the full correct T-matrix is used.

The same conclusion has been reached by Schaich (29,30) using an independent-electron evaluation of the equation (5). Schaich also extends his formalism to develop a framework for treating

29. Schaich, W.L., "Theory of the Driving Force for Electromigration", Physical Review B, Vol. 13, 1976, pp. 3350-3359.

30. Schaich, W.L., "Driving Forces for Electromigration by Linear Response", Physical Review B, Vol. 13, 1976, pp. 3360-3367.

more general defect centers. He also explicitly obtained the Faber formula (19) used by Stroud (20). An alternate version of the linear-response theory has been given (28) and used to explicitly verify Onsager's relation that Z^*e is the total flux of electrical charge associated with a unit flux of impurity.

Thus far, the results of linear-response calculations for specific systems appear to justify the following simplified procedure: One takes $\vec{F}_{es} = Ze\vec{E}$ and calculates $\vec{F}_{wd}$ on the basis of the charge density obtained from the electron wavefunctions in the absence of any electric field or current, but the occupancy of the electron states is obtained from the distribution function satisfying the Boltzmann transport equation. One need not determine δn from a self-consistent-field screening calculation as did BF provided that δn is assumed to act on the screened electron-impurity potential rather than on the bare potential in equation (3). This procedure reproduces Sham's results for the models he considered. Schaich (30) has derived a similar procedure.

Comparison with Experiment

Recent reviews emphasizing experimental data have appeared (31-33). Here we shall only mention a few important features.

According to equation (2) and the more general expressions which include band-structure and defect-structure effects in $\vec{F}_{wd}$, one expects

$$Z^* = Z[1 - \kappa/\rho] \qquad (6)$$

where κ, which arises from the electron wind, is independent of temperature. The above form seems to be in agreement with most data, though the magnitude of κ/ρ is often considerably larger than unity with the consequence that it has proven difficult to establish whether the direct electrostatic term is present.

First principles calculations of κ from pseudopotential theory

31. Rigney, D.A., "Electromigration in Metallic Systems", in Charge Transfer/Electronic Structure of Alloys, Bennett, L.H. and Willens, R.H., editors, The Metallurgical Society of AIME, New York, 1974, pp. 87-126.

32. Pratt, J.N. and Sellors, R.G.R., Electrotransport in Metals and Alloys, Diffusion and Defect Monograph Series, Trans Tech, Riehen, Switzerland, 1973.

33. d'Heurle, F.M. and Rosenberg, R., "Electromigration in Thin Films", Physics of Thin Films, Vol. 7, 1973, pp. 257-310.

were in fair agreement with data for a number of solid (6) and liquid (20) metals. Phase-shift estimates of κ were made for liquid metals (31) by assuming that κ was proportional to the total scattering cross-section for each species. The cross-sections were obtained from phase-shifts. The results are only semi-quantitative because no structural information is used. However, structure factors can be introduced along with phase shifts if one evaluates equation (5) using the "memory function" evaluation in a single-site T-matrix approximation (34). The result is the Faber formula with the pseudopotential replaced by a T-matrix in the phase-shift representation. The results, like Stroud's (20), give agreement with experimental observation on the concentration at which electromigration reverses in the Na-K system.

A correlation between the signs of κ and the Hall coefficient, R, is expected since in hole conductors the carrier-wind is opposite to its direction in electron conductors. Some correlation has been found for transition metals (3) but not for simple metals. This is not surprising since carriers in simple metals are predominantly free-electron-like. R, unlike $\vec{F}_{wd}$, however, is extremely sensitive to the relatively few electrons at the zone boundaries of simple metals where the Fermi-surface curvature is high. For metals having mostly small Fermi-surface parts, however, the carriers act as true electrons or holes for both R and $\vec{F}_{wd}$, and the correlation should persist. This apparently is the case for transition metals, where the sign of κ changes from plus to minus as the d-band fills across the periodic chart and is independent of impurity species in a given host metal (35).

From equation (6) one would expect a reversal of electromigration direction if κ is positive and if at higher temperatures ρ becomes larger than κ. Such reversals appear to have been observed (3). An explanation of the reversal in grain boundaries has been based on this idea (22), but the use of grain-boundary resistivity for ρ makes the argument dubious (35). It seems that understanding electromigration in grain boundaries may require an understanding of the motion and configuration of all atoms near the diffusing atom. This also seems necessary for understanding electromigration of fast diffusers (21) and isotope effects in hydrogen electromigration (35) and in liquid metals (19,20).

34. Sorbello, R.S. and Kumar, P.K., "Driving Forces for Electromigration in Liquid Metals", Bulletin of the American Physical Society, Vol. 20, 1975, p. 817.

35. Huntington, H.B., "Effect of Driving Forces on Atom Motion", Thin Solid Films, Vol. 25, 1975, pp. 265-280.

Driving Forces for Thermomigration

In general it is convenient to express the ion-current in terms of the heat of transport Q^* defined such that the ion current $\vec{J} = -DcQ^*\vec{\nabla}T/k_BT^2$. Now since $\vec{J} = \mu\vec{F}$, where $\vec{F}$ is the driving force, we have $\vec{F} = -Q^*(\vec{\nabla}T/T)$, which is analogous to the equation $\vec{F} = Z^*e\vec{E}$ for electromigration (35).

Electron Scattering Contribution

The driving force $\vec{F}$ arising from electrons is again given by equation (3) except that now the field $\vec{E}$ does not appear. In evaluating δn we must use the Fermi-distribution established by $\vec{\nabla}T$ rather than $\vec{E}$. This is the procedure followed by Gerl (18) using the charge-polarization model and by Fiks (36) and Huntington (37) using a ballistic model. Our discussion of the equivalence of these two models in electromigration extends here to thermomigration as well.

The calculation of $\vec{F}$ by Gerl (18) leads to

$$Q^* = \frac{2K_eT}{v_F} A \left[\frac{\partial \ln \rho_d}{\partial \ln E}\right]_{E_F} \qquad (7)$$

where K_e is the thermal conductivity, v_F is the Fermi velocity, A is the average cross-section for electron scattering at the Fermi energy E_F, and E is the electron energy. The logarithmic derivative, entering also in thermopower, implies a correlation between thermomigration and thermopower. This appears to exist in transition metals where both are large.

The physical interpretation of the Q^* result is that $\vec{\nabla}T$ causes hot (or fast) electrons and cold (or slow) electrons to flow in opposite directions. The net force depends on which electron wind-force is larger and this depends on the variation of the impurity cross-section, or ρ_d, with electron energy.

Many of the subtleties involved in Z^* are present in Q^*. In particular, local electron polarization around the bare ion might give rise to additional forces. It seems reasonable, however, in analogy with the electromigration case that these local-field

36. Fiks, V.B., "On the Thermodiffusion Mechanism in Fluids", Soviet Physics-Solid State, Vol. 3, 1961, pp. 724-726.

37. Huntington, H.B., "Driving Forces for Thermal Mass Transport", Journal of Physics and Chemistry of Solids, Vol. 29, 1968, pp. 1641-1651.

effects can be ignored if the full screened T-matrix is used in computing ρ_d.

To provide a more rigorous framework to address these questions, Kumar and Sorbello (38) have applied Luttinger's (39) linear-response technique to obtain the following result, exact to terms linear in $\vec{\nabla}T$, for the i-th component of force:

$$F_i = \left\langle\left\langle \frac{\partial V}{\partial R_i} ; \int h(\vec{r})\vec{r}\,d^3r \right\rangle\right\rangle \cdot \left(\frac{\vec{\nabla}T}{T}\right) \qquad (8)$$

where $h(\vec{r})$ is the energy density operator in the absence of the temperature gradient. This expression is the analogue of equation (5), and like that equation, may lead to fresh insight in understanding driving forces due to electron scattering.

Phonon Scattering Contribution

In general, we cannot expect that the concept of a microscopic force adequately describes all the effects of phonon currents. Here, however, we concentrate only on these microscopic forces.

We have shown that momentum or pseudo-momentum transfer by phonons in impurity scattering is not a relevant quantity (40). Such ballistic approaches are only valid for free impurities (e.g. neutrons) that are weakly coupled to the atoms comprising the phonon system. Atomic impurities in a solid, however, are localized and bound to their neighbors.

We have argued that a relevant force is the "phonon radiation force", which is the force associated with the shift in the equilibrium position of the impurity relative to the lattice (40). This force $\vec{F}$ turns out to be the average anharmonic force on the impurity during scattering. $\vec{F}$ is of the same order as the force which would be exerted on the impurity from a ballistic point of view. This is an accidental result arising from the fact that the Gruneisen parameter γ is of order unity. For perfectly harmonic lattices $\vec{F} = 0$ but the ballistic approach gives a finite rate of pseudo-momentum transfer. This is a spurious force since the atoms do not on the average go anywhere in a perfectly harmonic lattice.

38. Kumar, P. and Sorbello, R.S., unpublished.

39. Luttinger, J.M., "Theory of Thermal Transport Coefficients", Physical Review, Vol. 135, 1964, pp. A1505-A1514.

40. Sorbello, R.S., "Phonon Radiation Force in Defect Crystal Lattices", Physical Review B, Vol. 6, 1972, pp. 4757-4763.

Calculations for a linear-chain lattice model show that an interstitial impurity is pushed in the direction of the phonon wind (opposite to $\vec{\nabla}T$) if the impurity is heavier than the lattice atoms, and in the opposite direction if it is lighter (40). This may afford a possible explanation of some experiments in which impurities were found to move against $\vec{\nabla}T$. For relative mass-difference ϵ, we obtained a phonon contribution $Q^* = \epsilon\omega_D\tau\gamma k_B T$, where ω_D is the Debye frequency and τ is the phonon relaxation time. For vacancy migrations our estimate is $Q^* = (2/3)\omega_D\tau\gamma k_B T$. These expressions can lead to Q^* values of up to a few tenths of an eV, which is the typical magnitude of observed Q^*. It is quite possible however that the phonon-scattering contribution may be masked by the electron contribution (equation (7)) or by the so-called "intrinsic contribution" (35).

The various contributions to Q^* may often be small, and in addition, some cancellation is possible. This makes comparison with the small amount of existing data difficult (2,37). However, when the Fermi energy lies near a band edge of a high density-of-states band, the logarithmic derivative in equation (7) can be large, and the electron-wind (or hole-wind) effect will dominate Q^*. This has been advanced as an explanation of data on transition metals (2,18,37).

Conclusion

The theoretical situation for the driving forces for electromigration is promising. The recent linear response theory introduces a powerful new way of attacking the many-body aspects of the microscopic driving forces (13,17,28,30,41). Meanwhile, the semi-classical analyses (12,23,26,27,42) have added physical insight into the meaning of the various terms in the quantum-mechanical theories. Specific sources of the inhomogeneous local field have been identified, namely, the RRDs, CDM, and BF dipoles. Sham's result (13) indicates that the combined effect of all of these are automatically included in the scattering cross-section, or T-matrix, and are thus buried inside the electron-wind force. The question of how much is contributed by RRDs and CDM is difficult to determine and is still open to debate. Conceivably, one may also argue that the Langer prescription for electron-electron interaction as used by Sham is not sacrosanct, and that its use automatically tends to minimize the effect of the RRD field since the bare ion becomes screened in this prescription.

41. McCraw, R. and Schaich, W.L., "The Driving Force for Electromigration: Bootstrap Arguments", to be published.

42. Rorschach, H.E., "Dynamic Shielding of a Charge in a Metal", Annals of Physics, Vol. 98, 1976, pp. 70-86.

The great debate, in short, may have only just begun.

At this stage it seems that more refined experimental data is needed as well as more numerical calculations to test the theory. The existing first-principles calculations (6,20) gave fair agreement but need to be pushed further. If such calculations are to succeed, better characterization of impurity scattering pseudopotentials or T-matrices will be needed, and they should be able to explain both electromigration and electrical conductivity measurements at the same time.

Of particular interest are those systems in which Z^* shows anisotropy, isotope effect, and temperature or solute effects not expected on the basis of equation (2) or the more general form given by equation (6). In many cases only very approximate calculations will be feasible because of the many factors which generally enter into κ of equation (6). For the "jellium" model, κ equals $\rho_d Z_o N/ZN_d$, but in general band-structure and defect structure enter κ and ρ_d differently. Thus the direct connection between κ and ρ_d is broken, even though similar factors enter the expressions for both. Feit's expression, for example, gives κ as an integral involving impurity pseudopotentials, Bloch wave functions, and the anisotropic relaxation time over the Fermi surface (15). None of these quantities are generally known with accuracy, but nevertheless, one can still obtain some qualitative understanding of such phenomena as Z^* anisotropy without evaluating the integral precisely (43).

The theoretical situation for thermomigration is considerably less satisfactory than for electromigration. The theory of the electron-scattering contribution to thermomigration, however, promises to be developed to the same extent as the theory of the electron-scattering contribution to electromigration. In both cases the force derives from the electron charge density acting on the bare ion. One can expect refinements of the Gerl equation (7) for Q^* using the same techniques with which the Z^* equation (2) was generalized. In particular, we can obtain the extension of Feit's electron-wind force formula by replacing the electron distribution function for electrical conductivity by the distribution function for thermal conductivity. A rigorous treatment, however, requires evaluation of equation (8).

The phonon contribution to thermomigration has thus far only been crudely estimated by approximate evaluation of the "phonon radiation force". This force is of the same order as the force previously calculated (18) from a ballistic approach in which the

43. Chan, W.C. and Huntington, H.B., "Transport in Nearly-free-electron Metals. III. Application to Zinc", Physical Review B, Vol. 12, 1975, pp. 5441-5458.

phonons are assumed to transfer momentum as if a phonon of wavevector $\vec{q}$ possessed a momentum equal to the pseudomomentum $\hbar\vec{q}$ (40,44). The direction of the "phonon radiation force" may not necessarily be in the direction of the phonon current however.

It has yet to be convincingly proved that the "phonon radiation force", or any other microscopic force due to phonon scattering, for that matter, can be treated as a continuous force over the diffusion jump. The problem is that the motion of the impurity is not very slow with respect to the vibrations of the lattice atoms in the phonon system. For this reason, a collective impurity-phonon description of the diffusion jump (45) may be required in determining microscopic driving forces due to phonon scattering.

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44. Sorbello, R.S., "Radiation Pressure and Pseudomomentum of Quantum Excitations", Physics Letters, Vol. 53A, 1975, pp. 3-4.

45. Schottky, G., "A Theory of Thermal Diffusion Based on the Lattice Dynamics of a Linear Chain", Physica Status Solidi, Vol. 8, 1965, pp. 357-368.

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The current theoretical situation in electro- and thermomigration is reviewed. The physical basis underlying the driving force concept is discussed. A new linear-response expression is given for the electron-scattering contribution in thermomigration. The phonon-scattering contribution to thermomigration is also discussed.

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